Kinetics of Reactions in Solutions under Pressure. XXIII. The Base-Promoted Hydrolysis of Difluoramine. The Intermediacy and Behavior of Fluoronitrene[1]

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Abstract: The interception of an intermediate in the basic hydrolysis of difluoramine has been spectrophotometrically demonstrated by showing that "lures" undergo spectral changes in solutions of hydrolyzing difluoramine at rates compatible with the rate of disappearance of difluoramine. The lures have been shown to be inert to the buffers used, difluoramine itself, and its hydrolysis products. The major interception route seems to be *via* hydrogen abstraction: *N*-hydroxy-2,2,6,6-tetramethyl-4-piperidone (I) gives rise to the corresponding nitroxide II, benzene yields biphenyl, and thiophenol gives diphenyl disulfide. It has also been observed that the reaction of difluoramine with solid sodium hydroxide gives rise to chemiluminescence at a wavelength close to the known singlet–triplet transition of fluoronitrene and that the hydrolysis rate constant is unchanged over a concentration range of 10^6 in hydroxide ion. Together with the product array, these data suggest a mechanism involving difluoramide anion, fluoronitrene singlet, fluoronitrene triplet, and fluoramino radical.

We have previously[2] reviewed early suggestions (made mostly to explain products) concerning the intermediacy of fluoronitrene in various reactions. Craig, *et al.*,[3] have published a much more convincing argument for fluoronitrene. They found that the reaction of difluoroamine with base (first order in each) is several orders of magnitude faster than would be predicted by a Swain–Scott nucleophilicity plot. Interestingly, similar data first led Hine[4] to propose dichlorocarbene as an intermediate in the basic hydrolysis of chloroform. We have also measured the activation volumes[5] for the reaction of hydroxide and acetate with difluoramine, and compared them to the value of +16 cm^3/mol found for chloroform hydrolysis.[6] The reaction of hydroxide with difluoramine has an activation volume of +7 cm^3/mol, while the acetate displacement of fluoride from difluoramine yields an activation volume of −18 cm^3/mol.[2,7] These data can best be explained by Scheme I.

Scheme I

$$HNF_2 + OH^- \rightleftharpoons H_2O + NF_2^- \quad \text{(fast)}$$

$$NF_2^- \longrightarrow F^- + NF \quad \text{(slow)}$$

$$NF \longrightarrow \text{products} \quad \text{(fast)}$$

Craig[8] has also shown that the rate of production of fluoride ion from methyldifluoroamine and base is 35 times slower than from difluoramine under comparable conditions, and that the latter reaction is in turn much slower than the rate of deuterium exchange of difluoramine in heavy water.

Several features of the reaction continued to interest us. We hoped to add the trapping of fluoronitrene to the available evidence for that species. Since the nitrogen atom formally has only a sextet of electrons, the multiplicity is of interest. Martin[9] has published polarographic evidence for the existence of the difluoramide anion, and it appeared that an extension of the pH range over which the reaction rate was known would yield a value for the pK_a of difluoramine. Finally, while the reaction produces mainly *cis-* and *trans-*difluorodiazene, smaller amounts of nitrogen, nitrous oxide, and tetrafluorohydrazine are also observed.[10] In these products the nitrogen atoms are obviously not all in the same oxidation state, and any mechanism proposed must account for that. We continued our work on this reaction in the hope that we might resolve some of these questions.

Results and Discussion

It may be noted that while the reaction is first order in difluoramine, save for small amounts of nitrite and nitrate, all products contain two nitrogen atoms per molecule, even at difluoramine concentrations of 10^{-3} *M* or less. This fact reveals that a second molecule of difluoramine becomes involved only after the transition state has been traversed and that the intermediate thus implicated must be stable enough to survive a great many collisions with water molecules and buffer ions until, in effect, it is trapped by a second difluoramine molecule. This seemed to justify our hope that suitable trapping experiments might be devised.

Such experiments usually involve simply the diversion of a reaction by means of some compound (the "trap") to a new product in the structure of which the intermediate is still clearly recognizable. Actually, the mere occurrence of such a product does not prove the existence

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(1) Presented in part at the International Conference on the Mechanisms of Reaction in Solution, University of Kent, Canterbury, England, July 1970; this presentation was supported by a Graduate School Grant-in-Aid.

(2) W. J. le Noble and D. Skulnik, *Tetrahedron Lett.*, 5217 (1967).

(3) (a) A. D. Craig and G. A. Ward, *J. Amer. Chem. Soc.*, **88**, 4526 (1966); (b) W. T. Yap, A. D. Craig, and G. A. Ward, *ibid.*, **89**, 3442 (1967).

(4) J. Hine, *ibid.*, **72**, 2438 (1950).

(5) W. J. le Noble, *Progr. Phys. Org. Chem.*, **5**, 207 (1967).

(6) W. J. le Noble, *J. Amer. Chem. Soc.*, **87**, 2434 (1965).

(7) This negative value is larger than normal for displacement reactions (−5 to −10 cm^3/mol); this is undoubtedly due to pronounced electrostriction of the small fluoride ion. The difference between the positive values for the reactions of chloroform and difluoramine with hydroxide ion has the same explanation. See ref 5 for other examples of a correlation between ionic size and activation volumes.

(8) (a) A. D. Craig, private communications; (b) W. E. Becker and F. J. Impastato, *Advan. Chem. Ser.*, No. **54**, 132 (1966).

(9) K. J. Martin, *J. Amer. Chem. Soc.*, **87**, 394 (1965).

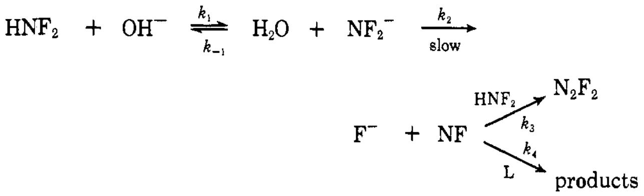
(10) G. A. Ward and C. M. Wright, *ibid.*, **86**, 4333 (1964).

of the intermediate, as the long and difficult search for free carbenes testifies.[11] An early search for a trap in the present reaction had only shown that the organic compounds used invariably gave rise to complex and intractable mixtures containing almost no bound fluorine, and that the nitrogen then appears exclusively as N_2.[8a]

In addition to this history, there are further reasons why this approach to trapping experiments did not seem attractive. The explosive nature of difluoramine (see Experimental Section), particularly in the presence of organic compounds and/or oxygen, mitigates against simply doing these early experiments on a larger scale. Furthermore, we felt that any positive results that might be achieved would be most significant if they applied to the same dilute, buffered aqueous solutions for which good evidence for fluoronitrene was already in existence. Few organic compounds are likely to be very soluble in such mixtures, thus further complicating product analysis. Therefore, we decided to concentrate not so much on the products, but rather on a search for compounds that would appear to be consumed somehow during the reaction, and on the kinetics of that consumption. Such compounds might be called "lures" more properly than "traps," since they operate not necessarily by incorporating the intermediate, but by diverting it from its normal path.

To deserve the designation lure (L), a compound must meet the following criteria: it must undergo some spectral change as the difluoramine hydrolyzes; this change must not take place in either acidic solution or in a spent solution (*i.e.*, it must not react with either difluoramine itself or with any of the normal products such as difluorodiazene); the change must be subject to the same rate law as is the disappearance of difluoramine alone. The rate constant will actually be smaller than in the absence of the lure by a factor which depends on the efficiency with which it competes with difluoramine itself for the intermediate (see Scheme II). The rate law becomes

Scheme II



$$\frac{-\mathrm{d}[\mathrm{HNF_2}]}{\mathrm{d}t} = \frac{k_1k_2[\mathrm{OH^-}][\mathrm{HNF_2}]}{k_{-1} + k_2}\left\{1 + \frac{k_3[\mathrm{HNF_2}]}{k_3[\mathrm{HNF_2}] + k_4[\mathrm{L}]}\right\}$$

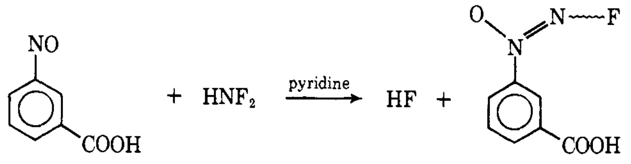
Thus, in the presence of various lures, pseudo-first-order rate constants may be observed that vary over a range of two, depending on the relative magnitudes of $k_3[\mathrm{HNF_2}]$ and $k_1[\mathrm{L}]$; they could in fact drift up or down over this range during a given run. The results are shown in Table I.

Table I. Second-Order Rate Constants[a] for the Spectral Changes of Several Lures at 25°

Lure	Spectral change obsd, λ, nm	mmol of L/mmol of HNF_2	k_2, l./(mol sec)[a]
III[b]	325 (incr)	0.2	1600
Benzoic acid	265 (incr)	0.2	1050
Benzene	340 (incr)	2	1210
Hexafluorobenzene	300 (incr)	1	1660
Acetone	300 (incr)	2	2000
Maleic acid	215 (decr)	1	1290
Methanol	See text	$>10^3$	960
Thiophenol	See text	4	2400
II[b]	See text	0.2	980

[a] $k_2 = k_1/[\mathrm{OH^-}]$. [b] See following text.

To be a candidate for investigation as a possible lure, a compound had to be somewhat soluble in and stable to the aqueous buffer solution (half-molar total phosphate at pH 7.20), and its concentration should be easily measured. Our first attempt involved *m*-nitrosobenzoic acid, nitroso compounds having been found by Stevens and Freeman[12] to react with difluoramine and pyridine in methylene chloride solution to give the corresponding N-substituted N^1-fluorodiimide *N*-oxides such as III. When difluoramine is decomposed in a phosphate buffer in the presence of *m*-nitrosobenzoic acid, the spectrum of the latter does undergo the expected initial change at the expected initial rate: the maximum at 322 nm disappears and gives way to a broad, featureless absorption tailing well into the visible region. However, the expected isosbestic points did not develop; secondary chemical reactions were clearly occurring and no rate constant could be obtained. We therefore used compound III itself and with it, as with the several other materials listed in Table I, we were able to determine first-order rate constants. The precision is only about 20% in some cases, but a variety of materials was used; all are stable in both acidic solutions of difluoramine and in basic solutions containing the normal hydrolysis products, and in the presence of hydrolyzing difluoramine all undergo spectral changes characterized by rate constants equal within a factor of two. This combination of facts is strong evidence for the capture of an intermediate in the hydrolysis.



The slowest rate observed in the presence of a lure was that with a large excess of methanol (7% by volume).[2] The difluoramine disappearance itself was observed in that case by means of polarography, and the methanol had served to give a smooth and reproducible wave; the fact that it is indeed a lure was demonstrated by the observation that benzene does not produce the bright yellow color normally generated by hydrolyzing difluoramine if excess methanol is also present.

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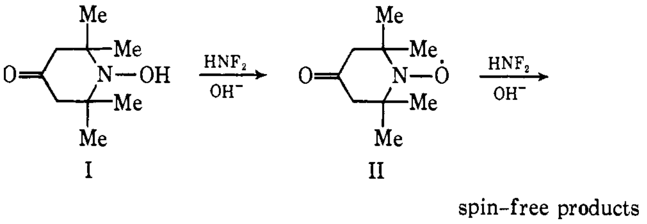
[11] R. A. Moss, *Chem. Eng. News*, **47**, 60 (June 16, 1969); **47**, 50 (June 30, 1969).

[12] T. E. Stevens and J. P. Freeman, *J. Org. Chem.*, **29**, 2279 (1964).

In two cases we also learned something about the nature of the products. From the experiments with benzene, small amounts of biphenyl (0–10%) could be isolated; tlc experiments revealed at least seven to eight colored spots in addition. Thiophenol gave a 100% yield of diphenyl disulfide; this compound precipitates from the solution as the reaction proceeds and this permitted a gravimetric analysis for the determination of the rate.[13] The nitrogen appears as N_2 if organic materials are present[8a] except in the case of thiophenol: since 4 mol of this compound is consumed per mole of difluoramine, the latter must be reduced all the way to ammonia. No attempts have been made to isolate products in any other case.

The conversions of benzene to biphenyl and of thiophenol to diphenyl disulfide suggest hydrogen abstraction as the mode by which fluoronitrene is diverted, and the experiment with 2,2,6,6-tetramethyl-4-piperidonoxyl (II) resulted from an attempt to prove that this is indeed the case. The precursor hydroxylamine, stable to both free difluoramine and to the normal hydrolysis products, in solution with hydrolyzing difluoramine immediately gives rise to the well-known triplet signal; the intensity of this signal rises to a maximum and then decays as additional fluoronitrene destroys the radical. Thus it is clear that hydrogen abstraction is indeed the reaction by which fluoronitrene proceeds, but further reaction prevented us from measuring the rate constant in that case. However, the radical itself can be prepared in pure form and hence used as a lure; the decay of the esr signal gives rise to a rate constant comparable with the others reported in Table I.



I

II

spin-free products

The hydrogen abstractions in turn suggest[14] that the nitrene being detoured is in the triplet state, although spin conservation requires that the species formed initially from difluoramide anion by loss of fluoride must be a singlet. Spin inversion is therefore occurring. The fact that fluoronitrene is isoelectronic with oxygen further reinforced our belief that the ground state must be a triplet.[15] Douglas and Jones[16] studied the emissions produced by the microwave discharge products of nitrogen trifluoride and assigned those occurring at 528.8 and 874.2 nm (the former much the more intense of the two) to the $X^3\Sigma^- \leftarrow b^1\Sigma^+$ and the $X^3\Sigma \leftarrow a^1\Delta$ transitions of fluoronitrene, respectively, in analogy to the transitions of oxygen. We were not able to detect these emissions from any solutions; however, it was observed that the introduction of gaseous difluoramine to an evacuated tube containing solid sodium hydroxide gave rise to a flash of visible light, the wavelength of which was determined by means of filters to be between 513 and 544 nm. More precise measurement is precluded for the moment by the awkwardness of the source. We also attempted to sensitize oxygen by means of hydrolyzing difluoramine, but the unfortunate circumstance that one or more of the normal products (probably difluorodiazene or tetrafluorohydrazine) mimic singlet oxygen in its ability to decolorize rubrene (adsorbed on silica) in the dark led to a result that can only be described as inconclusive.

The position of the preequilibrium poses a question that as yet is not completely settled. The pK_a of difluoramine is not known, but on the basis of the pK_a's of fluoroform (28), ammonia (35), and methane (40–58),[17] one would estimate no less than 15. If difluoramine is more acidic than that, then at high pH a substantial fraction would be in anionic form and the hydrolysis reaction would become essentially zero order in its base dependence. Our finding that several materials undergo spectral changes in the presence of hydrolyzing difluoramine made it possible to measure the rate at high pH by means of a stopped-flow apparatus. If benzene is used as the indicator of the progress of the reaction, the half-life of the difluoramine at 6.5° goes down to 50 msec at a pH of 13, and k_2 is found to have values of 130, 100, and 120 at pH values of 11.3, 12.0, and 13.0, respectively; the value that applies at pH 7.20 equals 50. This number is obtained by extrapolation from the values found at temperatures between 15 and 30° to 6.5° for the reaction in the presence of methanol at much higher ionic strength,[2] and it is therefore not rigorously comparable; nevertheless, the agreement is reasonably good, and the virtual constancy of k_2 over a hydroxide ion concentration range of nearly a million clearly indicates that difluoramine is still largely unionized at a pH of 13, and hence that its pK_a cannot be much less than 15.

There are some reports in the literature suggesting that difluoramine is more acidic and more stable at high alkalinity than our measurements and those of Craig[3] indicate. Martin[9] reported that the diffusion current of difluoramine can reversibly be reduced by an increase in pH, and interpreted this as due to its conversion to the anion. We confirm this observation, at least at pH values below 7, but the interpretation is apparently not unique; thus the species undergoing polarographic reduction might be protonated difluoramine, presumably present in exceedingly small equilibrium concentrations[18] (difluoramine is easily recovered from sulfuric acid; see Experimental Section). Martin furthermore claims that the diffusion current can be reduced to zero by adding excess base and that this decrease can be partially reversed by reacidification; we have not been able to duplicate this reversal, however. More recently, Dinwoodie, *et al.*,[19] reported that the pH of a 0.1 *M* so-

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[13] It is likely that thiophenol is oxidized to a minor degree by the normal hydrolysis products, which include a small amount of tetrafluorohydrazine;[3] this compound is known to be reduced by thiophenol to difluoramine: J. Freeman, M. Kennedy, and C. Colburn, *J. Amer. Chem. Soc.*, **82**, 5304 (1960). We did not observe it, however.

[14] For recent examples, see (a) R. A. Abramovitch and E. F. V. Scriven, *Chem. Commun.*, 787 (1970); (b) T. Shingaki, M. Inagaki, M. Takebayashi, R. Lebkücher, and W. Lwowski, *Bull. Chem. Soc. Jap.*, **43**, 1912 (1970); (c) R. J. Sundberg, M. Brenner, S. R. Suter, and B. P. Das, *Tetrahedron Lett.*, 2715 (1970).

[15] D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **40**, 2461 (1964). An MO scheme for fluoronitrene has been devised; see R. C. Sahni, *Trans. Faraday Soc.*, **63**, 801 (1967).

[16] A. E. Douglas and W. E. Jones, *Can. J. Phys.*, **44**, 2251 (1966); W. E. Jones, *ibid.*, **45**, 21 (1967).

[17] D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, pp 20 and 70.

[18] L. Meites, private communication.

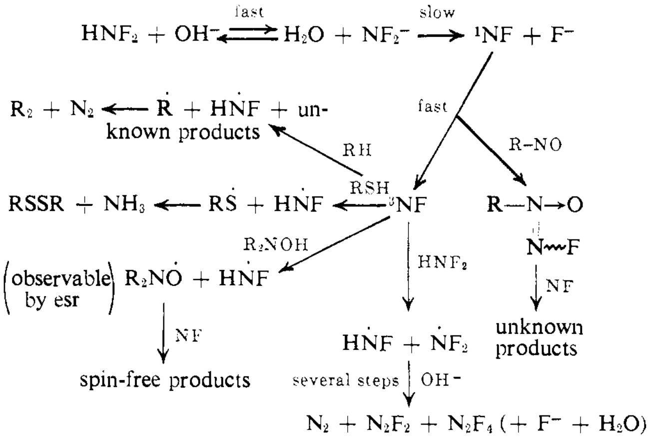
[19] A. C. Currie, A. H. Dinwoodie, G. Fort, J. A. Gibson, J. Grigor, J. B. Parker, and J. Peters, *J. Chem. Soc. C*, 1104 (1970).

lution of difluoramine is *ca.* 4, and deduced that the acid strength must be intermediate between those of hydrogen sulfide and hydrogen cyanide; the possibility that the low pH was due to hydrogen fluoride produced by hydrolysis was not considered. The authors were unable to isolate any salts. More important, they observed that after shaking difluoramine gas with 1 *N* hydroxide at 0° for 10 min, and after acidification and heating, 12% of this compound could be recovered from the solution. It is difficult to imagine an experimental error that could account for this result; however, we were able to show that the ability of aqueous difluoramine to produce a yellow color when benzene and hydroxide are *both* present is lost if strong base is added alone first, and that immediate subsequent neutralization does not regenerate this property (see Experimental Section).

It is conceivable that difluoramine *can* be regenerated from one of the hydrolysis products upon acidification, and that our failure to observe it only indicates that we have not exactly reproduced Dinwoodie's conditions for this reaction; however, it is hard to see how difluoramide ion can be responsible. It should be emphasized that the intermediacy and behavior of fluoronitrene are not in question—only the pK_a of difluoramine.

The minor products alluded to earlier (nitrogen and tetrafluorohydrazine) are easily accounted for in the following overall pathway, as further supported by the evidence described above (see Scheme III).

Scheme III



Several questions still remain, however, It would be of interest to know whether the initial trapping by nitroso compounds occurs at the singlet or triplet stage, how hexafluorobenzene detours the nitrene, what the precise wavelength of the emission is and what quenches it, how to explain the puzzling observations by Dinwoodie and Martin, and what preparative use can be made of the availability of virtual fluoronitrene solutions. Work on these questions continues.

Experimental Section

Materials. Difluoramine was prepared in more than 98% yield from trityldifluoramine and concentrated sulfuric acid by mixing them in a vacuum system.[20] The gas is pure as shown by the ir spectra[21] of samples obtained from traps held at various low temperatures. Solutions of difluoramine were prepared by condensing the gas on the surface of the degassed solvent frozen at −126° (methylcyclohexane slush bath) and subsequent melting. *Warning:* although solid difluoramine is known to detonate if cooled to 77°K, we have also experienced some explosions of liquid and gaseous difluoramine when samples were exposed to mild shocks such as might be imparted by a rapidly rising mercury surface. Small quantities of the material (<10 mmol) should be used unless special facilities are available; all work should be carried out behind safety shields.

The thiophenol, maleic acid, and benzoic acid used were reagent grade materials. Benzene of Spectrograde quality was subjected to two partial freezing operations. Hexafluorobenzene was shown by nmr to be free from any hydrogen-containing compounds. The preparations of ethyl *m*-nitrosobenzoate,[22] *m*-nitrosobenzoic acid,[22] and *N*-(*m*-carbethoxyphenyl) and *N*-(*m*-carboxyphenyl)-*N*′-fluorodiimide *N*-oxide[12,23] were carried out as described in the literature.

2,2,6,6-Tetramethyl-4-piperidonoxyl. A solution is made of 17.7 g of 2,2,6,6-tetramethyl-4-piperidine in 100 ml of water; a mixture of 38 mg of phosphotungstic acid, 2.73 g of sodium tungstate, and 2.40 g of disodium ethylenediaminetetraacetate is added. The mixture is treated with 50 ml of 30% hydrogen peroxide, allowed to stand for 4 days, saturated with sodium chloride, and extracted with three 250-ml portions of ether. The ether solution is washed three times with 1 *N* sulfuric acid and once with saturated aqueous sodium chloride, dried over sodium sulfate, filtered, and flash evaporated; the residual orange oil is dissolved in boiling hexane and allowed to crystallize: mp 46° (lit. 38° [24]); $a_N = 15.8$ G (lit.[24] 16 G). The corresponding hydroxylamine (mp 88–92°) was prepared by reduction of the radical with phenylhydrazine as described by Rozantzev;[25] it is somewhat unstable to oxygen and hence exhibited a weak signal due to the nitroxide radical.

High-Pressure Experiments. These have been described in sufficient detail elsewhere.[2]

Polarographic Experiments. See ref 3.

Kinetics and Trapping Experiments. An aqueous solution of 0.1 mmol of difluoramine in 25 ml of 0.5 *M* phosphate buffer at pH 7.12 was mixed with 25 ml of the same buffer saturated with benzene (~0.009 *M*) and 50 ml of additional buffer solution. The solution was kept at 25.0° in a large syringe. Samples were withdrawn at various times to record the uv and visible spectra. An absorption growing at 340 nm was used to determine the rate constant. The benzene spectrum remained unaltered if the pH was maintained at 4.0 or if the benzene-saturated buffer was not added until the difluoramine was completely hydrolyzed. Similar experiments were carried out with the other lures mentioned in the text.

If water saturated with benzene and 0.01 *M* aqueous difluoramine are added in that order to magnetically stirred 1.00 *M* sodium hydroxide (each 5.00 ml) at 0°, the bright yellow color characteristic of this reaction develops instantly; if 1 ml of this solution is added to 15 ml of water, the color is still unmistakable. If they are added to the base solution in the opposite order, no color is observable at all. If the difluoramine is added to the sodium hydroxide solution at 0°, the solution is acidified with 1.00 ml of 5.50 *N* sulfuric acid 5 sec to 10 min later, and the benzene and base solutions are then added, again no color can be discerned.

The benzene reaction was also carried out on a much larger scale, with benzene present as a second phase. The latter upon evaporation to small volume and tlc showed the presence of at least six products, all but one colored. The colorless product, isolated in 0–10% in several experiments, was identified as biphenyl. Thiophenol was converted by difluoramine in the presence of base to diphenyl disulfide, which quantitatively precipitated (1.97 mol of product per mole of difluoramine). Experiments with the other lure compounds were similar to that with benzene.

Stopped-Flow Experiments. The apparatus has been described.[26] A solution 10^{-3} *M* in difluoramine and 1.75×10^{-3} *M* in benzene

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[20] (a) W. H. Graham and C. O. Parker, *J. Org. Chem.*, **28**, 850 (1963); (b) A. U. Fokin and Y. M. Kosyrev, *Russ. Chem. Rev.*, **35**, 791 (1966).

[21] A. Kennedy and C. B. Colburn, *J. Amer. Chem. Soc.*, **81**, 2906 (1959).

[22] A. Schors, A. Kraaijeveld, and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, 74, 1243 (1955).

[23] T. E. Stevens, *J. Org. Chem.*, **33**, 855 (1968).

[24] R. Briere, H. LeMaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, 3273 (1965).

[25] E. G. Rozantzev and V. A. Godubev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 891 (1966); *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 852 (1966).

[26] G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

and made slightly acidic with hydrochloric acid was mixed at 6.5° with solutions 0.2 and 0.02 *M* in sodium hydroxide, or a phosphate buffer giving a pH of 11.3 upon dilution by an equal volume of water, in a Kel-F mixing chamber. The flow was stopped and the transmittance at 355 nm was displayed as a function of time on an oscilloscope screen. Photographs of the oscilloscope tracings were later used to calculate rate constants to a few per cent precision.

Electron-Spin Experiments. A dilute solution of I was prepared in a high-vacuum system in 5 ml of a phosphate buffer of pH 7.30. Half of this solution was sealed in an epr cell to serve as the reference intensity sample; the other half was made 0.01 *M* in difluoramine as described above. The frozen sample was warmed to room temperature and transferred under vacuum to an epr cell. The intensity of the signal in both cells was measured alternately for a period of 2.5 hr. The reference signal was constant to ±5%; the reaction sample quickly reached a maximum relative intensity of 4 (in 20 min), then gradually declined to 0.1 and less. If the aqueous solution used had already completely decomposed, the weak signal present at the beginning remained virtually constant in intensity over the 2-hr period it was monitored. A 2×10^{-3} *M* solution of the nitroxide was studied in a similar experiment; at a pH of 7.22 (phosphate buffer), a temperature of 25°, and a difluoramine concentration of 0.01, the signal decayed over a 2-hr period in first-order fashion.

Emission Experiments. A brief flash of visible light is emitted from the surface of sodium hydroxide pellets when these are exposed under vacuum to difluoramine gas; the flash is clearly observable through a Corning Glass No. 3-70 filter (cutoff at 513 nm), but not through the No. 3-67 filter (544 nm). A mercury-free vacuum system was used in these experiments. No emissions could be detected from solutions of difluoramine undergoing reaction with base.

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